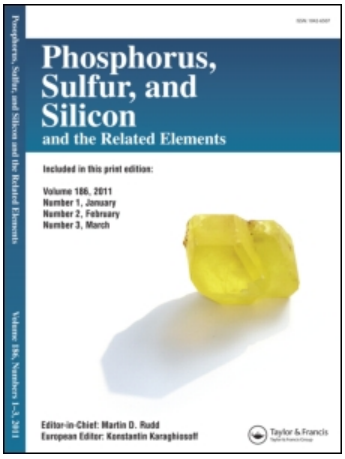

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NMR Studies of Restricted Rotation in Aminatophosphorus(1) Salts

Scott Thornburgh[a]; John L. Miesel[a]
[a] Discovery Research, Dow AgroSciences, Indianapolis, IN, USA

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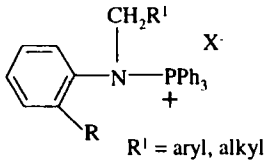
NMR Studies of Restricted Rotation in Aminatophosphorus(1+) Salts

SCOTT THORNBURGH and JOHN L. MIESEL

Discovery Research, Dow AgroSciences, Indianapolis, IN 46268, USA

A series of aminatophosphorus(1+) salts were synthesized as potential fungicides. Proton NMR of a set of compounds **1** within this series were observed to show selective line broadening of the methylene protons indicating a dynamic process which is slow on the NMR time scale. X-ray crystal structures of two of the compounds in the series showed a relatively planar nitrogen eliminating nitrogen inversion as the source of the observed line broadening. The methylene protons appeared as a sharp doublet ($^3J_{PH}$ = 3.6 Hz) at room temperature when R=OCH_3, a broad singlet when R=OCF_3, and a sharp multiplet consistent with the AB portion of an ABX (X = ^{31}P) spin system when R=SCH_3. Examination of the temperature dependence of the spectra revealed that the observed lineshape and temperature effects were consistent with slow rotation about the N-Ph bond and dependent primarily upon the size of the substituent R. Thus the slow rotation was thought to be due to steric factors and not the influence of electronic effects of the substituent R on the P-N bond. Rotation rates estimated from NMR lineshape analysis and plotted as a function of temperature for **1** when R = SCH_3 and R^1 = Ph gave an calculated energy barrier $\Delta G_{298}^{\dagger}$ of 17 kcal/mol. Similar studies for a variety of substituents R might be useful as a means of measuring relative steric bulk. At low temperature (ca. -50 °C) broadening of the PPh_3 resonances began to appear indicating a second independent dynamic process thought to be slow rotation about the N-PPh_3 bond on the NMR time scale at that temperature.



R^1 = aryl, alkyl

1